Freeze Concentration in Hazardous Wastewater Management

A combination of freeze concentration followed by incineration was the most cost-effective and environmentally friendly approach to manage the plant's hazardous wastewater.

The Challenge: Establishing the Best Hazardous Wastewater Management Approach

Niro Process Technologies B.V. needed to help a client find a hazardous wastewater management design for the client's chemical plants. Of special concern were the high-water content of the waste stream and the potentially hazardous volatile organic compounds (VOCs) it contains. The client wanted the design to be based on a technology that was proven, reliable, flexible, cost-effective, environmentally friendly, and safe. Several options were considered:

- **Bio-treatment systems** have been proven for many situations but in this case there were toxic components in the waste stream that can destroy flora.
- **Incineration** is the workhorse in the chemical industry and is capable of safely destroying a wide range of toxic components. However, it is expensive.
- **Super critical water oxidation** can destroy the organics and eliminates the need for a following bio-treatment system, but its maximum proven capacity is about 1 m^3/hr. At that scale, a cost-prohibitive 35 parallel reactors would be need.
- **Thermal wet air and catalytic wet air oxidation treatments**, which operate with high pressure (20 to 200 bar) (2,000 to 20,000 kPa) and medium temperature range (150°C to 350°C), have seen commercial service. In most situations they cannot completely destroy the organic components, but rather reduce the organic load by 75 to 80%. They also modify the nature of the organics so that a bio-treatment system can safely handle the waste. However, before commercial scale-up, each new waste needs rigorous oxidation and bio-system testing.
- **Evaporation and freeze concentration** (FC) are pre-treatment steps that can be used to reduce the overall costs of incineration by reducing the size of the waste stream requiring incineration. Evaporation is a well-developed unit operation with applications in many industries. Freeze concentration has been proven in over 50 commercial installations in the food industry.

The Old Way

The traditional approach would have been incineration, or evaporation and incineration. Usually evaporation is not considered whenever potentially hazardous VOCs are present. Wet air oxidation plus bio-treatment usually is too uncertain for untried compositions of hazardous wastes. FC followed by incineration was, at the time, a non-traditional approach that offered many benefits.

The New Way

In mid 1997, an Asian chemical plant started up the first full-scale application of FC for a hazardous wastewater application. The freeze concentration process is based on a proprietary special crystallization method combined with a mechanical separation technique (the wash column in Figure 1). The crystallization takes place in surface-scraped heat exchangers from which initially small crystals are supplied to recrystallizer vessels. The crystals grow to 100% pure spherical crystals in the recrystallizers (ripening effect). Their shape makes them ideal for separation from the concentrated liquid in the wash columns. Counter current washing with by-product water achieves separation. The end products are ultra pure water from the melted ice crystals and a non-diluted concentrate to be incinerated.

The Asian plant processes nearly 200,000 mt per year of wastewater (almost a 2 MW load). A second unit started up in September 1999 in Europe has double the capacity (3.5 MW load). The European complex uses five recrystallization units in series (each with its associated motor driven scraped surface heat exchanger crystallizer and motor driven recrystallizer stirrer) and seven wash columns in parallel (each with two motor driven proprietary mechanisms).

The design specifications and variable range for the first plant built using FC for this application is shown in Table 1. The second plant has flow rates about double those for the first, and similar compositions.

Table 1. Feed Stream Characteristics for Wastewater Stream at the Asian Plant

	Design	Range
Feed Rate – m^3/h	35	20-35
Concentration (split about 50/50 VOCs/salts) (%TSS)	5%	3% to 10% mainly change in organic composition
COD – mg/l	100,000	75,000 to 150,000

Table 2. Estimates of the Total Operating Costs for the Various Systems at the Asian Plant

	Approximate cost per m^3 feed
Thermal wet air oxidation & bio-treatment (both types)	$30-45
Catalytic wet air oxidation & bio-treatment	$35-50
Direct Incineration	$90-125
Evaporation & Incineration (total stream)	$70-95
Freeze Concentration & Incineration	$35-50

Table 2 shows estimated costs for the remaining viable options, for the first plant. The cases including wet air oxidation do not include costs for treating off gases, which generally need some further treatment.

Freeze concentration and incineration costs were projected to be similar to any of the viable oxidation steps and bio-treatment. However, FC and incineration had several advantages over the bio-treatment systems. It did not have to be proved out and did not require a costly holding pond or large surge vessels. It was more flexible and reliable relative to changes in both feed flow rate and composition, and it would not shut down due to random toxins. FC plus incineration also had less environmental impact and greater safety.

The selective nature of the crystallization process used in FC and the large bulk volume of the system allow for a wide variation in feed composition. The system also can easily absorb normal system fluctuations. Water, the bulk of the waste stream, is crystallized to ice. The rest of the solution plays a minor role in the concentration process.

Because of the high water content and volatile organic compounds, FC pre-concentration can significantly reduce the environmental impact of the incinerator. By reducing the amount of the feed to the incinerator, less fuel gas is consumed and less CO_2 is produced. An evaporator may also be used to concentrate the waste, but in the case of VOCs, the vapor will also need to be incinerated. The incinerator size cannot be reduced although the fuel gas consumption may be reduced since a portion of the feed is already vaporized.

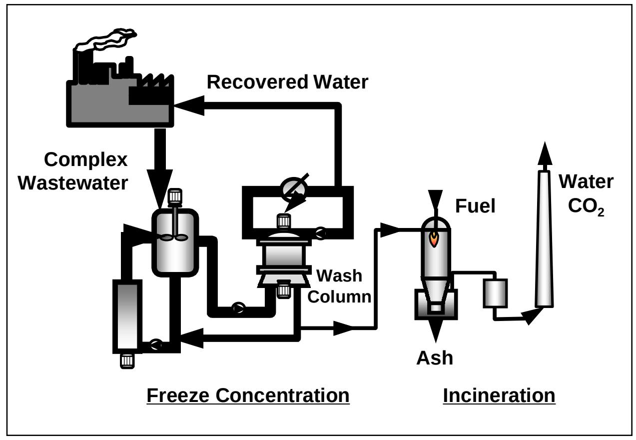

Figure 1. FC/Incineration Flow Diagram

The Results: A Cost Effective, Reliable, Flexible, and Environmentally Friendly Operation

Lower Costs. The FC plus incineration hazardous water management approach reduced operating costs relative to incineration and evaporation plus incineration. However, capital costs were similar.

More Environmentally Friendly. The system conserves water, uses less fuel, and ensures against inadvertent releases of VOCs.

What Did It Cost

FC plus incineration saves $50 to $75 per m^3 of feed relative to incineration and $35 to $45 per m^3 of feed relative to evaporation plus incineration. Since capital costs were similar, on an incremental basis, it had an infinite rate of return.

The Bottom Line: Economics Favor Freeze Concentration

When incineration is the only viable technical approach and hazardous VOCs are present, freeze concentration/incineration is the only viable economic approach. This assumes that electricity is available at reasonable rates.

Application Profiles

The combination of freeze concentration and incineration can be successfully applied to many aqueous waste streams. Present wastewater applications that have confirmed the feasibility of this unit operation in commercial operation include:

- Asian Plant Wastewater: caustic wash water, 18 mt/hour water recovery with <50 ppm total dissolved solids in recovered water, 1997
- European Plant Wastewater: caustic wash water, 34 mt/hour water recovery with <50 ppm total dissolved solids in recovered water, 1999

Photograph courtesy of Niro Process Technologies B.V.

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